[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE INHIBITION OF THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS. I[1]

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Many substances are known that inhibit the decomposition of hydrogen peroxide solutions, and some, such as acetanilide, phenacetin, benzamide, succinimide, phthalimide, etc.,[2] tannic acid and derivatives,[3] benzoic acid, salicylic acid, phthalic acid, etc.,[4] sulfanilic acid,[5] benzene sulfonic acid,[6] soap,[7] cinchonidine,[8] *p*-acetylaminophenol[9] and barbituric acid[10] may be used in commercial solutions as preservatives. Some of these substances were patented as early as 1906, principally for their inhibitive effect on the thermal decomposition. That they might have a similar action on the light decomposition does not seem to have been recognized until 1913 when Henri and Wurmser[11] presented a number of inorganic compounds that inhibited the light reaction, and in the following year Mathews and Curtis[12] added a number of organic and inorganic compounds. Recently Kailan[13] and Kornfeld[14] have studied the action of sodium hydroxide and sulfuric acid on the photochemical decomposition, and the latter has advanced a mechanism based on activated hydrogen and hydroxide ions and oxygen atoms, whereby the photocatalytic decomposition might take place in agreement with the known experimentally determined facts, and by which the inhibition by sodium hydroxide and sulfuric acid might be explained.

Miss Kornfeld's theory regarding the mechanism, however, does not explain why sodium chloride is a fairly good inhibitor whereas sodium sulfate hardly inhibits at all; or why a 0.000,025 *N* solution of mercuric chloride inhibits as strongly as a 0.05 *N* sulfuric acid solution; or why a 0.005 *N* benzoic acid solution inhibits more strongly than a 0.005 *N* hydrochloric acid solution, the latter surely yielding a much greater hydrogen-ion concentration.

[1] This is the first of two papers to be presented on the subject.

[2] U. S. pat., 825,883, July 10, 1906.

[3] U. S. pat., 946,529, Jan. 18, 1910.

[4] U. S. pat., 1,002,854, Sept. 12, 1911.

[5] U. S. pat., 1,025,948, May 7, 1912.

[6] U. S. pat., 1,058,070, Apr. 8, 1913.

[7] U. S. pat., 1,109,791, Sept. 8, 1914.

[8] U. S. pat., 1,128,637, Feb. 16, 1915.

[9] U. S. pat., 992,265, May 16, 1911.

[10] Ger. pat., 216,263, Apr. 27, 1909.

[11] Henri and Wurmser, *Compt. rend.*, **157**, 284 (1913).

[12] Mathews and Curtis, *J. Phys. Chem.*, **18**, 166, 521 (1914).

[13] Kailan, *Z. physik. Chem.*, **98**, 495 (1921).

[14] Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).

Mathews and Curtis, in determining the relative efficiency of a number of substances, failed to observe any properties possessed in common, and came to the conclusion that the action of the inhibitors could be explained only when the mechanism of catalysis in general was understood. This is the point at which they left the subject in 1914, and with the exception of the two papers mentioned above, no further work has yet been published.

The problem of inhibition might, it was thought, be studied more successfully by a more systematic examination of inhibitors than had been made by either Henri and Wurmser, on the one hand, or by Mathews and Curtis on the other. It was planned, therefore, to study the effect of inhibitors more particularly from the standpoint of their constitution and of the physical properties associated with such constitution, especially the absorptive power. Thus, for example, by a study of the inhibitory powers of benzoic acid and of derivatives of the acid such as the esters, or of compounds closely allied with benzoic acid, one might be able to associate the inhibitory powers with definite groupings in the molecule, or with the absorptive capacity which these exerted.

Organic inhibitors,[15] on this basis, would inhibit the photochemical decomposition of hydrogen peroxide by virtue of their ability to rob the hydrogen peroxide molecules of radiant energy. The progress of the work showed that this alone was insufficient to account for all the cases of inhibition studied. The possibility of compound formation between peroxide and inhibitor was indicated with accompanying complexities due to possible absorption of energy (1) by the organic compound (2) by a compound formed between a non-absorbing organic compound and the peroxide or (3) by both.

Inhibitors of the first class should function only in the region of wave length within which they absorb; those of the second class would be expected to function throughout the entire ultra-violet range effective for hydrogen peroxide, for their absorption depends upon the hydrogen peroxide residue; third class inhibitors should function as the second class and in addition should exhibit increased inhibition in the wave region within which the organic molecule itself absorbs.

It may be pointed out that if absorption be the cause for the inhibition, a hydrogen peroxide solution containing no stabilizer should be inhibited if the radiation be first passed through a solution of the stabilizer, *i. e.*, the inhibition may be due to a screening effect. Such is indeed the fact if a solution of the inhibitor of sufficient concentration and thickness be used. However, as will be shown later, if an inhibitor of the same concentration be employed first in a screening solution and then in the peroxide solution as an inhibitor, the thickness of the screen being not much greater

[15] Only organic inhibitors will be considered in this paper; the inorganic and a general summary are reserved for Part II.

than that of the peroxide solution, the rate of decomposition in the first instance will be considerably greater than that in the second, and this is true even if the screening solution itself be of hydrogen peroxide.

In the protection of rubber from "perishing," when exposed, for example, as thin sheets in balloon fabrics, by the addition to the rubber of suitable dyes, it has been shown by Porritt,[16] that the effect is due entirely to the screening effect. The divergence between this case and our results with hydrogen peroxide is, we feel, of importance, and should be accounted for in any successful interpretation of the work.

Experimental

The present investigations were conducted with 25 typical organic compounds, whose ultra-violet absorption spectra have been carefully examined by Baly and other workers. Three ultra-violet wave regions were obtained by employing glass filters similar to those described in Bulletin No. 148, U. S. Bureau of Standards,[17] in Curves 68, 69 and 78. A fourth wave region was secured by using the full transparency of the apparatus which was entirely of quartz.

The decomposition of hydrogen peroxide by ultra-violet light has been shown by both Tian[18] and Henri and Wurmser[19] to be a monomolecular reaction. So if one represent by C' the velocity constant, defined for a reaction of the first order, for the decomposition of a hydrogen peroxide solution containing no added stabilizers, under a constant illumination of a definite region of wave length and at a constant temperature, C'' the velocity constant for the decomposition of the preceding solution containing a definite amount of inhibitor, C'' being determined under precisely the same conditions of illumination and temperature as C'; then $C'' \times 100/C' = K$, the inhibition constant. For solutions of hydrogen peroxide containing substances that do not inhibit, $K = 100$; for solutions containing stabilizers, K is less than 100; the smaller the value of K, the stronger the inhibition. The value for K depends on the concentration of the inhibitor and the region of wave length. This constant is a measure of the efficiency of an inhibitor and affords a means of comparing the relative values of stabilizers.

Apparatus.—The reaction vessel consisted of a transparent quartz cylindrical tube, 45 cm. long, and of 2.5 cm. internal diameter, sealed at one end, provided at the open end with a brass collar and wooden pulley and at the closed end with a brass cap fitted with an iron plunger. This tube rotated in another transparent quartz cylinder provided at the lower closed end with a metal bearing. Water was pumped through this outer jacket from a thermostat. By this means the peroxide solution under investiga-

[16] Porritt, *Trans. Faraday Soc.*, **16**, Appendix, 83 (1920).

[17] Gibson, Tyndall and McNicholas, Bur. Standards, *Tech. Paper*, **148** (1920).

[18] Tian, *Compt. rend.*, **151**, 1040 (1910).

[19] Henri and Wurmser, *ibid.*, **157**, 126 (1913).

tion was easily maintained at a constant temperature of 25°. Slight changes in temperature have no detectable effect on the rate of decomposition as the temperature coefficient is small.[12,14,20]

The source of illumination was a Hanovia quartz mercury-vapor arc lamp, operated on a 100 volt d. c. circuit, and burning at 3 amperes, and 50 or 70 volts. In series with the lamp was a sliding resistance of about 15 ohms, and a d. c. ammeter; in parallel was a 100 volt d. c. voltmeter. The lamp gave a 7cm. arc and was operated in a vertical position, parallel to the upright reaction vessels, and 35 cm. from them. The illumination became constant 15 minutes after lighting. Between the lamp and the reaction tube there was a movable wooden partition provided with a slit 12 cm. high and 4 cm. wide which served as a window for the illumination. This window could be closed by means of a shutter. It could also be fitted with the glass filters for providing the different regions of wave length.

The quartz apparatus was transparent to ultra-violet radiation as far as 2000 Å., whereas the apparatus used by Mathews and Curtis[12] could transmit only to 2500 Å. Coblentz and Kohler[21] have shown that 30% of the radiation from a quartz mercury vapor arc lamp is in the ultra-violet, and that of this, only 6% is of wave lengths shorter than 3000 Å. It is principally this 6% that the hydrogen peroxide absorbs.[20] Consequently, apparatus of maximum transmission was very desirable. In addition, the use of a quartz reaction tube eliminated the chance of the peroxide solutions being contaminated with dissolved alkalies. For this same reason quartz or wax apparatus was used in handling all solutions.

The Hydrogen Peroxide Solutions.—Conductivity water, of specific conductivity 1.09×10^{-6}, was at first employed, but it was found that once distilled water, of specific conductivity about 6×10^{-6}, stored in a silica bottle, gave practically identical results, and so the latter was used in preparing all solutions.

A commercial 30% hydrogen peroxide, free from inhibitors, was poured from a wax container into a quartz flask and diluted so as to give a solution that was from 2 to 5% hydrogen peroxide. This solution contained traces of impurities as was shown by comparison with 2 hydrogen peroxide solutions made by different methods. However, these impurities should not affect the values for the inhibition constants. The comparative solutions were made as follows.

a.—Method of Pietzsch and Adolph.[22]—Pure recrystallized potassium persulfate was distilled with sulfuric acid and water in a vacuum, the liberated hydrogen peroxide distilling as fast as formed, according to the reactions, $K_2S_2O_8 + H_2SO_4 \longrightarrow K_2S_2O_7 + H_2SO_5$ (Caro's acid); $H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$; $K_2S_2O_7 + H_2O \longrightarrow 2KHSO_4$. As the distillation proceeded, water was added from a dropping funnel so as to keep the total volume in the distillation flask constant. The condenser consisted of a quartz tube within a water jacket, and led into a Bunsen suction flask coated within with paraffin. Starting with 100 g. of potassium persulfate, 67 g. of sulfuric acid (d. 1.6), and 50 cc. of water, the distillate, about 200 cc., contained about 5% of hydrogen peroxide.

b.—Hydrated barium peroxide or sodium peroxide was treated with a cold solution of 1–5 sulfuric acid, filtered, and the filtrate distilled in a vacuum.

Procedure for Determination of Inhibition Constants

Sixty-six cc. of 2 to 4% hydrogen peroxide solution free from inhibitors was placed in the reaction tube, and the tube clamped in an upright position

[20] Tian, *Ann. Physik*, **5**, 248 (1916).

[21] Coblentz and Kohler, Bur. Standards, *Sci. Paper*, **378**, 233 (1920).

[22] Pietzsch and Adolph, Brit. pat., 23,660, 1910. Skirrow and Stein, *Trans. Am. Electrochem. Soc.*, **38**, 206 (1920).

in the quartz water-jacket and rotated on a bearing by a pulley system and a motor to stir the solution. The window in the partition between the lamp and the reaction tube was provided with the proper filter to give the region of wave length required and was closed with the shutter. The mercury arc was then started and the sliding resistance regulated so as to give the desired drop of potential, 50 volts, across the lamp. Water was pumped through the water jacket surrounding the reaction vessel to maintain it at a uniform temperature of 25°. After the illumination had become constant, about 0.5 g. of the peroxide solution was pipetted into a weighed weighing-bottle containing a little sulfuric acid, which prevented thermal decomposition, and when the solution had attained the temperature of the balance, weighed, transferred to a beaker containing an excess of sulfuric acid, and titrated with 0.05 *N* potassium permanganate solution. The shutter in the window was then removed, and the time of removal noted to the nearest half minute. From time to time samples were removed, and the concentration of hydrogen peroxide determined as above, the time of sampling in each case being noted. The velocity constant was calculated at every titration from titer to titer, using the equation for the first order.

The procedure for determining the rate of decomposition of hydrogen peroxide solutions containing inhibitors was exactly the same. It is to be remembered, however, that many of the inhibitors react with potassium permanganate. Consequently, in order to obtain reproducible results it was necessary that the weight of sample taken each time be as nearly uniform as possible, and that the titrations be made under similar conditions. With these precautions, while the percentage of hydrogen peroxide found may in each case be a trifle too high, the difference between the logarithms, which is of primary interest, will also in each case be the same over the short intervals employed, as if the stabilizer did not react with the titration agent.

The principal source of error was in the titration, and in particular in the reading of the buret. This had to be done with the greatest care, the nearest 0.01 cc. being estimated; otherwise the velocity constants obtained varied considerably, and the results were of little value. It was, of course, essential that the buret used be very carefully calibrated. The other important error, that in weighing, could be easily maintained at a minimum. By careful work it was usually possible to determine the concentration of a 3% solution to within 0.003%, or 0.1%. This means, however, that two velocity constants may differ by as much as 20%; the average of a number of determinations of the same constant, nevertheless, would probably be within 5% of the correct result. As the inhibition constant is the quotient of two velocity constants multiplied by 100, this may vary from the true value by as much as 10%; that is, if the

inhibition constant is found to be 9, the correct value may be 10 or 8; if found to be 80, it may be 72 or 88 or any value between these two. It is, therefore, seen that the smaller values for this constant experimentally determined are more likely to be correct than the larger, which may be considerably in error. It is to be noted that slight error in the standardization of the permanganate solution does not affect the relative percentages and, therefore, the value for the velocity constant, provided the same permanganate solution be used throughout the determination.

It was found that after a 2 to 4% solution of the peroxide had been made up and stored in a wax bottle, the rates of decomposition, under like conditions, of portions of the solutions were identical, although determinations were made several weeks apart. One example is given below to show the constancy of the velocity constant.

TABLE I

RATE OF DECOMPOSITION OF TWO TO FOUR PER CENT. HYDROGEN PEROXIDE (Without inhibitor)

Time Min.	Concn. H_2O_2 %	$C' \times 10^6$	Time Min.	Concn. H_2O_2 %	$C' \times 10^6$
0	4.107	..	125	3.063	2550
29	3.881	1950	138	2.969	2390
47	3.721	2330	159	2.821	2420
71	3.510	2430	174	2.722	2400
92	3.325	2570			Av. 2400
112	3.167	2430			

As the hydrogen peroxide can be activated only by those wave lengths which it absorbs, and as the absorption of the peroxide relative to that of the inhibitor must always be considered, it is essential that, before proceeding further, the absorption of the peroxide itself be briefly considered. Hartley[23] as early as 1881 showed that hydrogen peroxide solutions absorbed but little of the ultra-violet above 2920 Å. Henri and Wurmser[24] have determined by spectrographic and thermo electric-pile methods the molecular extinction coefficients for hydrogen peroxide at a number of wave lengths. These are as follows: for $\gamma = 2800$, 2558, 2300, 2100 and 2060 (the wave lengths in Ångström units) molecular extinction coefficients = 3.0, 20, 75, 127 and 127, respectively.

The averages of a number of determinations of C'', the velocity constant of the solution containing inhibitor, and of C', the velocity constant for the same solution without inhibitor, together with the value for K, the inhibition constant, for a typical few of the 25 substances investigated, are given in Table II. In almost all cases, determinations were made for 4 different regions of wave length extending in each case from the visible spectrum to lower limits corresponding to 2000, 2650, 2930 and 3050 Å., respectively.

[23] Hartley, *J. Chem. Soc.*, **39**, 111 (1881).

[24] Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913).

In making comparisons, it is to be remembered that only the inhibition constants are comparable and that the concentration of the inhibitor and the strength of its absorption at that concentration must always be considered. It was established that the inhibition constants were independent of the variations in velocity of decomposition of the uninhibited hydrogen peroxide solutions of the purity obtainable in any of our stated methods of preparation. The most probable impurities, acids and alkalies, are themselves inhibitors.

TABLE II

DECOMPOSITION AND INHIBITION CONSTANTS OF TYPICAL SOLUTIONS

Acid	Conc. M	Region of wave lengths Å.	$C'' \times 10^6$	$C' \times 10^6$	K
Acetic	0.005	to 2000	1050	1450	72.4
		2650	404	412	98.0
		2930	227	232	97.8
		3050	99	99	100.0
Phenylacetic	0.001	to 2000	190	1450	12.9
		2650	193	412	46.8
		2930	181	232	78.0
		3050	99	98	101.0
Hydrocinnamic	0.0033	to 2000	414	3460	11.9
	approx.	2650	380	982	38.7
		2930	385	550	70.0
		3050	201	200	100.3
Benzoic	0.005	to 2000	212	2400	8.8
		3050	199	200	99.5

The experimental results compiled from such data for K, the inhibition constant, are collected in Table III for all the substances examined. The values have been rounded off as a comparison of Tables II and III will show, in a manner consistent with the accuracy of experiment previously stated.

TABLE III

GENERAL SUMMARY OF INHIBITION CONSTANTS

Substance	Conc. M	Regions of wave length to 2000	to 2650	to 2930	to 3050
Acetic acid	0.005	75	100	100	100
Phenylacetic acid	0.001	13	45	80	100
Hydrocinnamic acid	0.003 approx.	12	40	70	100
Benzoic acid	0.005	9	...	...	100
Ethyl acetate	0.005	100	100	100	100
Ethyl benzoate	0.001 approx.	14	50	80	100
Ethylphenyl acetate	0.001 approx.	17	70	85	100
Ethyl cinnamate	0.0002approx.	25	45	65	100
Methyl oxalate	0.005	10	20	35	70
Methyl benzoate	0.005	9	...	...	...
Ethylamine	0.005 approx.	5	0	0	0
Aniline	0.005	7	0	0	0
Benzylamine	0.005	8	0	0	0
Acetamide	0.005	65	100	100	100

Benzamide	0.003	9	...	...	...
Acetanilide	0.0001	60	100	100	100
Ethyl alcohol	0.005	35	35	35	35
Phenol	0.002	0	0	0	0
Benzyl alcohol	0.0033	approx. 8	25	40	40
Acetone	0.005	70	60	55	50
Acetophenone	0.0002	11	40	65	100
Benzophenone	0.0001	45	60	100	100
Benzene	0.005	20	...	70	...
Quinine hydrochloride	0.0002	9	20	10	0
Quinine salicylate	0.0002	4	0	0	0

The values of K may be interpreted as follows: 80 to 100, extremely weak or no inhibition; 50 to 80, weak inhibition; 30 to 50, moderate inhibition; 20 to 30, fairly strong inhibition; 10 to 20, strong inhibition; 0 to 10, very strong inhibition.

These results may now be treated in detail from the standpoint of the relationship between absorption and inhibitory power. The materials used will be discussed under the general headings of the compound type to which they belong. A few details as to purity of sample, location and character of the absorption, behavior towards hydrogen peroxide and ultra-violet light will be given in each case.

Acids.—*Acetic acid;* m. p., 16.4°. In aqueous solution of the strength employed, absorption begins at about 2600 Å.[25,26,27] The absorption is weak throughout the range with which these experiments are concerned.

Benzoic acid, high grade, recrystallized once from water, absorbs strongly from 2860 Å. downward with but 30 mm. of a 0.005 M aqueous solution.[28,29,30,31]

Hydrocinnamic acid, m. p., 47.2°, absorbs quite strongly from 2750 Å. in a 0.0033 M solution 150 mm. thick.[32,33,34,35]

Phenylacetic acid, m. p., 76.4°, absorbs very strongly in dilute aqueous solution from 2750 Å. downward. There is a particularly strong band at 2700 Å., the molecular extinction coefficient being 1100.[29,32,35]

Berthelot and Gaudechon[36] have shown that with these acids in dilute aqueous solution and for short illuminations the decomposition by ultra-violet light is negligible.

It is evident that light absorption and inhibitory power are parallel in the case of the acids studied. Acetic acid shows weak absorption and little inhibition. Phenylacetic acid shows the strongest absorption and the greatest inhibitory action of the four in the most dilute solution.

[25] Hartley and Huntington, *Phil. Trans.*, **170**, 257 (1879).

[26] Hantzsch and Scharf, *Ber.*, **46**, 3570 (1913).

[27] Bielecki and Henri, *Compt. rend.*, **155**, 456, 1617 (1912); **156**, 550 (1913); **157**, 372 (1913); **158**, 567 (1914); *Ber.*, **45**, 2819 (1912); **46**, 1304, 2596, 3627 (1913).

[28] Hartley and Hedley, *J. Chem. Soc.*, 91, 319 (1907).

[29] Purvis, *ibid.*, **107**, 966 (1915).

[30] Strasse, *Z. wiss. Phot.*, **14**, 281 (1915).

[31] Hantzsch, *Ber.*, **49**, 226 (1916).

[32] Baly and Collie, *J. Chem. Soc.*, **87**, 1332 (1905).

[33] Stewart, *ibid.*, **91**, 199 (1907).

[34] Wright, *ibid.*, **103**, 528 (1913); **105**, 669 (1914).

[35] Baly and Tryhorn, *ibid.*, **107**, 1058 (1915).

[36] Berthelot and Gaudechon, (a) *Compt. rend.*, **151**, 478 (1910); (b) **152**, 376 (1911).

It was at one time thought that the formation of per-acids or of double compounds between the acids and aqueous hydrogen peroxide might cause complications. The work of R. y Miró[37] renders the former improbable. While aqueous hydrogen peroxide is a weak acid[38,39,40] it is extremely unlikely that in the dilute solutions employed any marked compound formation occurred.

Esters.—*Ethyl acetate* (b. p., 77°) absorbs in the ultra-violet only from 2300 to 2330 Å. and this band is extremely weak.[41] *Methyl benzoate* (b. p., 198.9°) absorbs strongly below 2890 Å.[42] *Ethyl benzoate* (b. p., 313.2°) absorbs strongly below 2900 Å.[35] *Ethylphenyl acetate* (b. p., 227.3°) absorbs very little above 2600 Å. in dilute solution, the upper limit of the absorption band being at 2800 Å.[32,35] *Ethyl cinnamate* (b. p., 226.7°), shows absorption even in 0.0001 *M* aqueous solution below 3030 Å., there being a strong band from 3000 to 2500 Å.[35,42] *Methyl oxalate* was recrystallized from water. It shows increasing absorption with decrease in wave length. At 2300 Å. the absorption is very strong. A 0.005 *M* solution transmits to 2940 Å. through 100 mm. thickness.[27,34,43]

Conductivity measurements employing a quartz cell and tin electrodes showed no appreciable hydrolysis of ethyl acetate or ethylphenyl acetate in 4 hours of illumination. To eliminate as much as possible any effect due to hydrolysis, a fresh solution of ester in the peroxide solution was used every 4 hours. Decomposition of the esters by ultra-violet light in the time exposed is negligible at the dilution employed.

The results as to inhibition show good concordance with the absorptive capacities of the several esters. Ethyl acetate the weakest absorbent shows no inhibition over the entire range. The others inhibit in about the proper proportions in the various regions of wave length. It is of interest to compare the effects of benzoic acid and of methyl benzoate. Both show similar absorption curves and similar inhibitory effects in comparable concentrations.

Amines.—*Ethyl amine* used was a 33% solution. It absorbs only very weakly between 2190 and 2480 Å.[44]

Aniline (b. p., 183.8°) absorbs continuously below 3120 Å. in a 0.005 *M* solution 80 mm. thick. There are strong bands between 2850 and 2740 Å. and between 2400 and 2300 Å.[32,35,45,46]

Benzylamine (b. p., 187.1°) absorbs feebly from 2740 to 2290 Å. and strongly below 2290 Å.[45]

Ethylamine and benzylamine are not affected appreciably by ultra-violet light under the conditions of experiment.[36] Aniline in peroxide solutions quickly becomes reddish-yellow when exposed to ultra-violet radiation, presumably by oxidation. Among oxidation products Gibbs found azobenzene, dianilino-quinone, dianilino-quinone anil and azophenine.[47,48]

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[37] R. y Miró, *Anal. Fis. Quim.*, **18**, 35 (1920). *J. Chem. Soc., Abst.*, [2] **118**, 483 (1920).

[38] Calvert, *Z. physik. Chem.*, **38**, 513 (1901).

[39] Joyner, *Z. anorg. Chem.*, **77**, 103 (1912).

[40] Lewis and Randall, THIS JOURNAL, **36**, 1987 (1914).

[41] Bielecki and Henri, *Physik. Z.*, **14**, 520 (1913).

[42] Baly and Schaefer, *J. Chem. Soc.*, **93**, 1808 (1908).

[43] Crymble, Stewart, Wright and Rea, *ibid.*, **99**, 1262 (1911).

[44] Bielecki and Henri, *Compt. rend.*, **156**, 1861 (1913).

[45] Purvis, *J. Chem. Soc.*, **97**, 1546 (1910).

[46] Ley and Ulrich, *Ber.*, **42**, 3440 (1909).

[47] Gibbs, THIS JOURNAL, **34**, 1190 (1912).

[48] Freer, *Philippine J. Sci.*, **5B**, 1 (1910).

Comparison of inhibition and absorptive capacity here shows no regularity. With the 3 amines in the wave regions above 2650 Å. the inhibition constants are zero, *no* decomposition of the peroxide being measurable after 2 hours' illumination. For aniline this might have been associated with the strong absorption which it shows, but this is not so with the other 2 amines whose absorption is weak. It must be remembered, however, that the amines in aqueous solution form bases and so may be behaving as does sodium hydroxide[11,12] which, though diactinic to ultra-violet light[49] is, nevertheless, a strong inhibitor. It is possible that this inhibition is due to interaction between the bases and hydrogen peroxide functioning as a weak acid.[38]

Amides.—*Acetamide* (m. p., 82.1°) absorbs below 2690 Å., the absorption being weak and very similar to that of acetic acid.[50]

Benzamide (m. p., 130.5°) has practically the same absorption as benzoic acid, 30 mm. thickness of 0.005 *M* solution absorbing below 2890 Å.[28]

Acetanilide (m. p., 111.7°) absorbs strongly below 2600 Å. even in 50 mm. of a 0.0001 *M* solution.[42,51]

The concordance in these examples between absorption and inhibition is good. In the wave regions above 2650 Å., in which neither acetamide nor acetanilide absorbs at the concentrations employed, the inhibition is negligible. The concordance between benzamide and benzoic acid is to be emphasized. Evidently any effect such as was found with the basic amines is here absent.

Alcohols.—*Ethyl alcohol*, specially purified and dried for use, is practically diactinic over the whole ultra-violet range.[25,27,52,53] *Benzyl alcohol* (b. p., 205°) absorbs moderately below 2700 Å.[35] *Phenol* (m. p., 41.9°) in a 0.005 *M* solution of thickness 17 mm. begins to absorb at 2850 Å. with a strong band between 2830 and 2610 Å.[54,55,56,57] A solution of phenol in hydrogen peroxide becomes yellow even in the dark; in the light the change is very rapid.[58,59] The products of oxidation include quinol, catechol and *p*-benzoquinone.[47,48,60] Catechol[54,56] and quinol[56,61] absorb very similarly to phenol. *p*-Benzoquinone absorbs continuously from 5000 Å. and very strongly below 3500 Å.[61,62]

Ethyl and benzyl alcohols retard decomposition to a greater extent than would be expected from the absorption data. Benzyl alcohol inhibits most strongly in that region of wave length in which the alcohol absorbs. Both alcohols show marked retardation in regions in which they do not absorb to any degree. It is possible that retardation is due to esterification of hydrogen peroxide acting as a weak acid, though we have no proof of this. With a freshly prepared 0.005 *M* alcohol solution the rate is first fast but quickly decreases to a minimum at which it remains constant. This might be due to compound formation such as suggested.

[49] Wright, *J. Chem. Soc.*, **103**, 532 (1913).
[50] Ref. 44, p. 1860.
[51] Baly, Tuck and Marsden, *J. Chem. Soc.*, **97**, 571 (1910).
[52] Nutting, *Phys. Rev.*, **13**, 193 (1901).
[53] Henri, *Ber.*, **46**, 2650 (1913).
[54] Baly and Ewbank, *J. Chem. Soc.*, **87**, 1347 (1905).
[55] Hartley, Dobbie and Lander, *ibid.*, **81**, 929 (1902).
[56] Purvis and McCleland, *ibid.*, **103**, 1088 (1913).
[57] Witte, *Z. wiss. Phot.*, **14**, 347 (1915).
[58] Hanko, *Ber.*, **25**, 386 (1892).
[59] Kohn and Fryer, *J. Soc. Chem. Ind.*, **12**, 107 (1893).
[60] Martinon, *Bull. soc. chim.*, **43**, 155 (1885).
[61] Hartley and Leonard, *J. Chem. Soc.*, **95**, 34 (1909).
[62] Baly and Stewart, *ibid.*, **89**, 502 (1906).

Phenol inhibits the decomposition of hydrogen peroxide in all wave regions, the inhibition constants being zero. The strong absorption of *p*-benzoquinone probably accounts for this strong action.

Ketones.—*Acetone*, obtained from bisulfite compound, boiled at 56.5°. It shows weak absorption throughout the whole region below 3300 Å. The maximum absorption is at 2650 Å. Below 2650 Å. absorption becomes weaker and at 2140 Å. the solution is diactinic.[24,63,64,65,66,67] Its decomposition in dilute solution in ultra-violet light is neglibible[66,69] under the given conditions. Acetophenone (b. p., 200–204°) absorbs strongly in 250 mm. thickness of 0.0002 *M* solution below 2940 Å.[32,35,56] Benzophenone (m. p., 48.6°) absorbs moderately below 2850 Å. in 300 mm. thickness of even a 0.0001 *M* solution. The phenones do not react appreciably with hydrogen peroxide solution.[70]

Acetone constitutes an exception to normal inhibitory influence which is of importance in the correlation of absorption and inhibition. Its inhibitory influence, unlike most of the others, is strongest in the upper region of wave length. The absorption of acetone with respect to hydrogen peroxide is stronger in the upper region than in the lower. In the lower region where the hydrogen peroxide absorbs the strongest, the acetone hardly absorbs at all. It would be expected, therefore, that the value for the inhibition constant over the entire region, 3940 to 2000 Å., would be greater than that for the region 3940 to 2930 Å.; that is, the inhibition is stronger in the upper region than over the entire region. The experimentally determined values agree with this. The inhibition in all regions is weak but is somewhat stronger in the upper region.

Acetophenone and *benzophenone* inhibit about as would be expected from absorption data. Were they more soluble, they would probably be excellent inhibitors as, in concentrated solutions, they absorb over the entire range of the ultra-violet.

Benzene and Alkaloids.—*Benzene* probably containing a trace of thiophene was used. A thickness of 100 mm. of a 0.005 *M* solution absorbs from 2650 Å. with a strong band between 2650 and 2310 Å.[32,71] The solution became slightly yellow on exposure to ultra-violet light, due to partial oxidation by the peroxide.[72,73] The products are quinone, quinol and catechol.[73] Ultra-violet light alone will not decompose benzene.[36b]

Quinine hydrochloride absorbs strongly from 3850 to 2970 Å., weakly from 2970 to 2870 Å., and strongly below 2720 Å. in even a 20 mm. thickness of 0.0002 *M* solution. It is important to observe that the solution is practically diactinic between 2870 and 2720 Å.[74,75]

The absorption spectrum of quinine salicylate has not been determined. Hantzsch has shown[76] that the general nature of absorption is not affected to any large extent by formation of molecular compounds, provided the process is not accompanied by a change

[63] Bielecki and Henri, *Ber.*, **47**, 1690 (1914); Ref. 41, p. 516; *Compt. rend.*, **158**, 567, 1022 (1914).

[64] Brannigan, Macbeth and Stewart, *J. Chem. Soc.*, **103**, 406 (1913).

[65] Henderson, Henderson and Heilbron, *Ber.*, **47**, 876 (1914).

[66] Rice, THIS JOURNAL, **42**, 727 (1920).

[67] Purvis and McCleland, *J. Chem. Soc.*, 101, 1810 (1912).

[68] Pastureau, *Compt. rend.*, **140**, 1592 (1905).

[69] Baudisch, *Biochem. Z.*, **103**, 59 (1920).

[70] Nicolet and Pelc, THIS JOURNAL, **43**, 935 (1921).

[71] Hartley, *Phil. Trans.*, **208A**, 475 (1908); *Z. wiss. Phot.*, **6**, 299 (1908).

[72] Curtis, THIS JOURNAL, **42**, 720 (1920).

[73] Cross, Bevan and Heiberg, *Ber.*, **33**, 2015 (1900).

[74] Dobbie and Fox, *J. Chem. Soc.*, 101, 77 (1912).

[75] Dobbie and Lauder, *ibid.*, **99**, 1254 (1911); **83**, 605 (1903).

[76] Hantzsch, *Ber.*, **50**, 1413 (1917).

in molecular constitution. Assuming, therefore, that the absorption of quinine salicylate is approximately the sum of the absorptions of quinine and salicylic acid we should expect continuous absorption below 3400 Å.[34,74,75] The salicylic acid should eliminate the diactinic portion of the region of wave length noted under quinine hydrochloride. There is no evidence in the case of either quinine salt of any decomposition during illumination.

The inhibition results are readily correlated with the absorption data. Benzene is a weak inhibitor in the upper region where it does not absorb. Some of this effect may even be due to absorption by the small amount of quinone produced. In the case of quinine hydrochloride the existence of the diactinic region between 2870 and 2720 Å. is evidenced by the correspondingly high value for the inhibition constant in the experiment including these wave lengths, namely, that for the region above 2650 Å. This disappears in the case of quinine salicylate as expected. Of all the inhibitors tried, quinine salicylate is by far the best as regards photochemical decomposition.

Screening Experiments

A solution of hydrogen peroxide containing no inhibitors was placed in the reaction vessel and maintained at 25° by a stream of water pumped, through the outer jacket, from a thermostat. Radiation from the quartz mercury-vapor arc lamp was passed through an empty quartz tube of about 5 cm. internal diameter, and then into the reaction vessel, which was about 2.5 cm. in internal diameter. The rate of decomposition of the hydrogen peroxide was measured. A solution of hydrogen peroxide of approximately the same strength as that in the reaction tube and containing sufficient quinine salicylate to make the solution 0.0002 *M* was placed in the tube between the light source and the reaction vessel, the apparatus being so arranged that all the light received by the pure hydrogen peroxide solution must pass through the solution containing inhibitor. The rate of decomposition of pure peroxide solution was again determined. The rate of decomposition of the peroxide solution containing the inhibitor, 0.0002 *M*, had already been measured, and so, from the inhibition constant, the rate at which the solution should decompose under these conditions could be calculated. For pure peroxide, without screening the solution, a velocity constant of decomposition of 0.000352 was found; with screening, 0.000103; and for peroxide solution with inhibitor (calc.), 0.000013. The values for the inhibition constants are, 30 with screening solution, 3.7 with inhibitor in the peroxide solution.

A similar experiment was made with 0.005 *M* benzoic acid, except that in this case the screening solution contained no peroxide. The pure peroxide without screening gave 0.000219; with screening, 0.000129; and peroxide solution with inhibitor (calc.), 0.000019. The values for the inhibition constants are, 60 with screening solution, 9 with inhibitor in the peroxide solution.

It is evident from these results that screening the solution of hydrogen peroxide by means of an outside bath of a solution of the inhibitor is by no means as effective as the placing of the inhibitor in the solution of the per-

oxide. This result is in marked contrast to the experiments of Porritt already cited.[16]

Henri and Wurmser[19] have shown that Einstein's law of photochemical equivalence is not applicable to the decomposition of hydrogen peroxide, 1 "*hν*" being able to effect the decomposition of a number of molecules. Kornfeld,[14] in attempting to disprove this, finally concluded that 1 "*hν*" could decompose as many as 80 molecules of hydrogen peroxide, and explained it by a mechanism by which the activation is passed on from molecule to molecule.

The explanation of the ability of an inhibitor to function more efficiently when in the peroxide solution than when acting in a screening solution possibly lies in this ability of 1 quantum to decompose more than 1 molecule. Thus, if the stabilizer be acting as a screening solution, the peroxide being free from inhibitors, 1 quantum of light energy may slip through, enter the peroxide solution, and by successive activation decompose a number of molecules. On the other hand, if the stabilizer be in the peroxide solution, and 1 quantum of radiation should succeed in activating a peroxide molecule, this molecule will decompose, liberating again the quantum. This may activate another peroxide molecule or, coming within the sphere of influence of a molecule of inhibitor, may be converted into more harmless infra-red.

Summary

1. The inhibitory effects of 25 typical organic compounds on the photochemical decomposition of hydrogen peroxide solutions have been studied in 4 definite spectral regions of the ultra-violet.

2. The inhibition by such agents has been associated with the absorptive capacity of the organic compounds for ultra-violet light. A striking correlation between these two factors has been obtained in the case of benzene, several esters, acids, amides, ketones and alkaloids. The retarding action of amines and alcohols requires an explanation based on other causes than absorption.

3. It has been shown that the inhibitors act more efficiently when in the peroxide solution than when in a screening solution of similar thickness and concentration. A possible reason for this has been advanced.

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